

# HYDROGEN PERMEABILITY OF TANTALUM-BASED MEMBRANE MATERIALS AT ELEVATED TEMPERATURE AND PRESSURE

*K.S. Rothenberger<sup>1</sup>, B.H. Howard<sup>1</sup>, A.V. Cugini<sup>1</sup>, R.M. Enick<sup>2</sup>, F. Bustamante<sup>2</sup>, M.V. Ciocco<sup>3</sup>, B.D. Morreale<sup>3</sup>, and R.E. Buxbaum<sup>4</sup>*

<sup>1</sup>U. S. Department of Energy, National Energy Technology Laboratory (NETL), P.O. Box 10940, Pittsburgh, PA 15236

<sup>2</sup>NETL Research Associate, University of Pittsburgh

<sup>3</sup>NETL Support Contractor, Parsons Project Services, Inc.

<sup>4</sup>REB Research and Consulting

## Introduction

Literature data indicates that tantalum, with a properly activated surface, may be a suitable component of a hydrogen separation membrane. The solubility of hydrogen in tantalum, based on literature data between 625-944 K and 0-107 kPa [1], was correlated by Steward [2] as (Equation 1):

$$S(H_2/Ta) = 0.132 \exp\left(\frac{4050}{T[K]}\right) \frac{\text{mol}}{\text{m}^3 \text{Pa}^{0.5}} \quad (1)$$

A critical review of diffusion coefficient data from literature was cited by Steward [2] in his review of the permeability of metals as (Equation 2):

$$D(H_2/Ta) = 4.4 * 10^{-8} \exp\left(\frac{-1620}{T[K]}\right) \frac{\text{m}^2}{\text{s}} \quad (2)$$

The product of Equations 1 and 2 was used to estimate the hydrogen permeability of tantalum [2] as (Equation 3):

$$K(H_2/Ta) = 5.8 * 10^{-9} \exp\left(\frac{2430}{T[K]}\right) \frac{\text{mol}}{\text{msPa}^{0.5}} \quad (3)$$

Although the upper temperature limits of the solubility and diffusion coefficient limits are 944 K and 573 K, respectively, graphical representations of this correlation extrapolated to 1000 K can be found in the literature [3,4]. Equation 3 indicates that the permeability of tantalum decreases with increasing temperature because the diffusion coefficient increases with temperature more slowly than the hydrogen solubility decreases.

Direct permeability measurements of palladium-coated tantalum membranes at low to moderate pressure (20-373 kPa) have been reported [3,5]. Permeation experiments were also conducted on bulk tantalum [6], but the results of this internal document were reported in the open literature in terms of diffusion coefficient [7]. The permeability of the tantalum membranes under these conditions was less than the value provided by the extrapolation of the correlation provided in Equation 3 to the temperatures of interest.

The objective of this study was to evaluate the hydrogen permeability and surface behavior of tantalum and palladium-coated tantalum materials under a wide range of temperatures (up to 1173 K) and pressures (up to 2.8 Mpa) in order to assess their viability as components in hydrogen separation membranes.

## Experimental Section

**Membrane Fabrication.** Bulk tantalum membranes were fabricated by punching 16 mm diameter disks out of a 1 mm thick, 99.9% pure, tantalum sheet. Tantalum was cleaned using an acid mixture of 20 vol-% HNO<sub>3</sub>, 20 vol-% HF, and 60 vol-% H<sub>2</sub>SO<sub>4</sub> in order to remove surface oxides and contaminants before testing and or coating. Tantalum membranes were coated with a thin palladium layer in one of three ways. An electroless plating method, previously described by Buxbaum [3,5,8], was used to deposit a 1-2 micron thick coat of palladium on tantalum at the laboratory of REB Research and Consulting. A sputter coating method, developed at NETL, was used to deposit a thin (average thickness = .04 micron) palladium coating. A modified version of the same method was used to deposit a thicker (average thickness = 1.2 micron) palladium coating. In all cases, both sides of the tantalum disk were coated. Selected membranes were characterized by optical microscopy, scanning electron microscopy (SEM), and xray photoelectron spectroscopy (XPS), before and after testing.

**Permeability Testing.** The hydrogen membrane testing (HMT) unit was designed and constructed at NETL and is described elsewhere [9,10]. The typical membrane unit feed gas consisted of a mixture of 10 percent helium in hydrogen. An argon sweep gas was used to minimize the concentration of hydrogen on the permeate side of the membrane. The hydrogen in the permeate stream was quantified with a gas chromatograph.

Permeability testing was done at temperatures ranging from 623 K to 1173 K. Total feed pressures ranged up to 2.8 Mpa from atmospheric. Permeability values were calculated based on a flux analysis that used a hydrogen partial pressure exponent of 0.5 to facilitate comparisons with previous investigators. However, actual best fit measurements of the exponent ranged from 0.21 to 0.83.

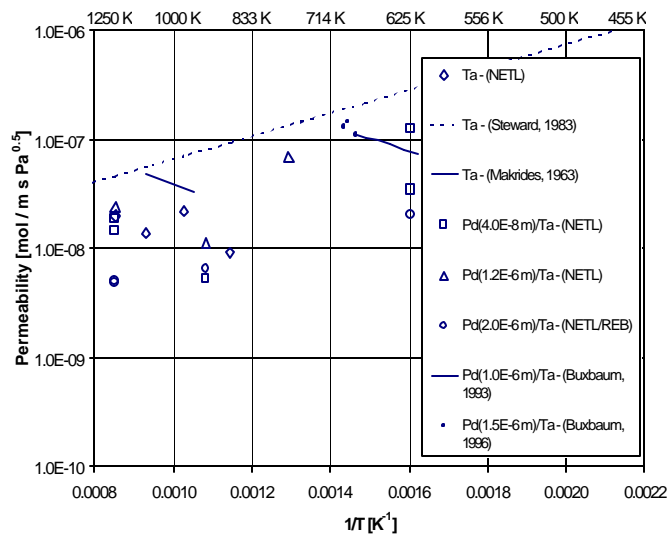
## Results and Discussion

**Bulk Tantalum.** A series of bulk tantalum membranes were tested in the temperature range from 873 - 1173 K. The results are shown in Figure 1. Permeability values fell well below that predicted from the extrapolated Steward correlation [2], and were somewhat less than those of Makrides et al [6], which were measured over a smaller temperature range. The temperature dependence of the data was quite scattered, but showed a general trend to higher permeability at increased temperature, in agreement with that recorded by Makrides [5] and Buxbaum [6] and opposite that predicted by Steward [2]. In all cases, equilibration time was relatively slow, with tests taking up to two weeks in duration. In spite of the cleaning procedure used before testing, it appeared that some surface contamination occurred over the course of the long test duration, probably altering the characteristics of the membrane. Tantalum is known to be subject to contamination, particularly via oxidation.

**Electroless Plated Tantalum.** The electroless plated palladium-coated tantalum membrane was tested for 28 days, the longest single test of any tantalum-based membrane. During this time, it was subjected to the full range of test conditions at temperatures of 623 K, 923 K, and 1173 K, and pressures up to 2.8 MPa. Equilibration times were still quite slow, particularly at the lower temperatures. Permeability values at these three temperatures

are shown in Figure 1. The results were approximately an order magnitude below the extrapolated Steward correlation and less than those obtained from the bulk tantalum test. However, the temperature dependence of the permeability was quite linear and nearly parallel to that predicted by Steward, with lower permeability at higher temperature.

The surface of an electroless plated membrane was characterized before and after testing. Prior to testing, surface palladium coverage ranged from 50-80%, with one side showing higher coverage than the other. After testing, the feed side of the membrane was highly eroded, with much evidence of material loss with spalling from the surface in layers. Generally, no palladium was detected with the



**Figure 1.** Permeability of tantalum and palladium-coated tantalum.

exception of several small areas near the edges. Tantalum was the primary element detected with varying amounts of oxygen and carbon. The sweep side was also rough and porous with cracking, but without the material loss seen on the feed side. Palladium still covered much of the tantalum surface, with small amounts of carbon and oxygen impurities. Although there is no data available to confirm this, the slow equilibration times of the membrane would seem to indicate that the palladium coating may have been lost early in the testing process.

**Sputter Coated Tantalum (Thin Film).** A series of four test runs were made using a bulk tantalum disk sputter-coated on each side with a “thin” (average thickness = .04 micron) palladium film. The first two tests were made at 623 K and atmospheric pressure. These runs yielded the two points shown on the right side of Figure 1. One of these points yielded the highest measured permeability of any tantalum-based membrane tested at NETL. Although both points fell slightly below the Steward correlation, they were similar to values recorded on palladium-coated tantalum membranes by Buxbaum [3] in a similar temperature range. For both membranes, attempts to change the test condition resulted in sudden failure. Microscopic examination of the membrane revealed significant cracks in the surface as well as an apparent phase change in the tantalum metal. The formation of a tantalum hydride phase, known to be brittle, is assumed to have occurred. However, as of this writing, it has not yet been experimentally verified. The two other “thin”

sputter-coated membranes were tested at 1173 K, and 923 K-1173 K, respectively, with maximum permeability values plotted in Figure 1. Each sample showed an initial rise in flux followed by a longer decay. Characterization of the surface after testing showed no palladium present. It is believed that the decay in measured flux corresponded to a loss of the palladium coating and concomitant increase in surface resistance to hydrogen permeation.

**Sputter Coated Tantalum (Thick Film).** A series of three test runs were made using a bulk tantalum disk sputter-coated on each side with a “thick” (average thickness = 1.2 micron) palladium film. The goal of these experiments was to see if the palladium film thickness influenced the permeation behavior of the membrane. The three membranes were tested at 773 K, 923 K, and 1173 K, respectively. Test duration varied between 48-94 hours. The membranes tested at 773 K and 923 K were relatively stable throughout the duration of testing. However the membrane tested at 1173 K showed a slow decay in measured flux beginning almost immediately. The maximum values of permeability are listed in Figure 1. Surprisingly, characterization of the surface after testing showed little palladium present, regardless of the temperature at which testing occurred. Characterization of these membranes is ongoing.

Taken as a group, the permeability values for both the “thin-Pd” and “thick-Pd” sputter coated membranes fall within a range below that predicted by the Steward correlation, and above that recorded for the electroless Pd-plated membrane. The scatter inherent to the data made it difficult to ascertain a distinct temperature dependence of the permeability.

## Conclusions

A series of bulk tantalum and palladium-coated bulk tantalum membranes were tested for hydrogen permeability over a temperature range of 623-1173 K, and a pressure range from atmospheric to 2.8 MPa. The measured permeability values fell below that predicted by the extrapolated Steward correlation by as much as one and a half orders of magnitude. The combined effects of diffusion constant reduction at elevated pressure, surface contamination in our continuous high pressure apparatus, and the significant differences between the temperature-pressure conditions of the Steward correlation and our study contributed to this difference. At 623 K, coating of the bulk tantalum metal with a thin palladium film resulted in relatively high hydrogen permeability, but with likely formation of a tantalum hydride phase and failure of the membrane. At 773 K and above, a palladium film coating did not appear to influence the measured hydrogen permeability. Surface characterization performed following testing showed little palladium left on the tantalum surface. However, the palladium film may have at least temporarily protected the tantalum surface from fouling, as the experimental results from the palladium-coated tantalum generally showed both a smaller degree of scatter than that from uncoated bulk tantalum and a quicker response to changes in test conditions.

**Acknowledgement.** This work was supported by the “Transportation Fuels and Chemicals” and “Gasification Technologies” product lines of the U.S. Department of Energy’s Office of Fossil Energy.

## References

- (1) Veleckis, E.; Edwards, R.K. *J. Phys Chem*, **1969**, 73, 683-692.
- (2) Steward, S.A.; "Review of Hydrogen Isotope Permeability Through Metals," Lawrence Livermore National Laboratory Report UCRL-53441, August 15, 1983.
- (3) Buxbaum, R.E.; Kinney, A.B.; *Ind. Eng. Chem. Res.* **1996**, 35, 530-535.
- (4) Moss, T.S., Peachey, N.M., Snow, R.C., Dye, R.C., *Int'l J. Hydrogen Energy*, **1998**, 23 (2) 99-106.
- (5) Buxbaum, R.E.; Marker, T.L. *J. Membrane Science*, **1993**, 85, 29-38.
- (6) Makrides, A.; Wright, M.; McNeill, R. Final Report for Contract DA-49-189-AMC-136(d); Tyco Lab, Waltham, MA, **1965**.
- (7) Volkl, J.; Alefeld, G. In *Diffusion in Solids, Recent Developments*; Nowick, A.S. and Burton, J.J., Eds. Academic Press, New York, NY, 1975, pp. 232-295.
- (8) Buxbaum, R.E.; Hsu, C.Z. U.S. Patent 5,149,429, Sept. 22, 1992.
- (9) Morreale, B.D., *Evaluation of Inorganic, Hydrogen Membranes at Elevated Temperatures and Pressures*, M.S. Thesis, University of Pittsburgh, 2001.
- (10) Rothenberger, K.S.; Cugini, A.V.; Siriwardane, R.V.; Martello, D.V.; Poston, J.A.; Fisher, E.P.; Graham, W.J.; Balachandran, U.; Dorris, S.E. *Prepr. Pap. - Am. Chem. Soc. Div. Fuel Chem. Div., Prepr. Pap.*, **1999**, 44(4), 914-918.